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STUDIES OF THE OPTICAL PROPERTIES OF SOME ORGANIC CRYSTALS

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ABSTRACT. The directions of the optical principal directions of the monoclinic crystals anthraquinone and naphthalene tetrachloride have been determined for three different wave-lengths in the green, yellow and red regions of the spectrum. The principal refractive indices for these wave lengths have been determined for the crystals of anthraquinone meta-dinitrobenzene, phloroglucine dihydrate and naphthalene tetrachloride.

INTRODUCTION

The optical properties of crystals have attracted the attention of physicists and minerologists from very early days of science. Recently the subject is receiving renewed interest owing to its importance in the determination of the atomic arrangements inside crystals. This can particularly be said about aromatic organic crystals where the optical properties give indications of the orientations of the benzene rings inside the crystals. Accordingly, a systematic investigation into the optical properties of organic crystals have been undertaken in this laboratory.

Of the four crystals that we have studied, two, namely, anthraquinone and naphthalene-tetrachloride belong to the monoclinic system and other two, namely metadinitrobenzene and phloroglucine dihydrate belong to the orthorhombic system. So, for the former crystals it has been necessary to determine the directions of the principal axes, while in the latter they are fixed along the directions of the crystallographic axes. For the monoclinic crystals, however, the monoclinic axis is one of the principal axes while the other two, which are at right angles to each other, lie in a plane normal to this axis. For the determination of the directions of these basal axes, the crystal was mounted on Fedorov stage, placed between crossed nicols of a polarising microscope, and the crystal was rotated about the direction until extinction was observed. The angle between the direction of the electric vector of the polarised light and a crystal edge is measured accurately and hence the directions of the principal axes are fixed. For the determination of the principal refractive indices, the Becke method has been utilised. For this purpose the crystal is immersed in a drop of a liquid, whose refractive index is intermediate between two principal indices of the crystal, and is mounted on the Fedorov stage with the plane containing the two principal directions normal to the axis of the optical system. The crystal is illuminated by pola-

rised light and is rotated about the axis of the optical system until the Becke line just disappears. This is repeated for another liquid of intermediate refractive index. The two principal refractive indices α and β are given by the relation,

$$(i)\quad \alpha^2 = \frac{n_1^2 n_2^2 \cos^2\theta_2 \sin^2\theta_1 - n_1^2 n_2^2 \sin^2\theta_2 \cos^2\theta}{n_1^2 \sin^2\theta_1 - n_2^2 \sin^2\theta_2}$$

$$(ii)\quad \beta^2 = \frac{n_1^2 n_2^2 \cos^2\theta_1 \sin^2\theta_2 - n_1^2 n_2^2 \cos^2\theta_2 \sin^2\theta_1}{n_1^2 \cos^2\theta_1 - n_2^2 \cos^2\theta_2}$$

where n_1 and n_2 are the refractive indices of the two liquids and θ_1 and θ_2 are the angles between the first principal axis and the directions of the electric vectors for the disappearance of the Becke lines.

In some crystals it is not convenient to determine all the three refractive indices by this method. In such cases the optic axial angle is determined on the Fedorov stage. This gives us a further relation between the principal refractive indices, α, β and γ,

$$\frac{\gamma}{\alpha}\sqrt{\frac{\alpha^2-\beta^2}{\beta^2-\gamma^2}} = \mathrm{Tan}V_a$$

where V_a is half the optic-axial angle

All the measurements were carried out for three parts of the spectrum namely, red, yellow and green. Red light was obtained from an incandescent electric lamp by filtering through two parallel walled glass vessels, (each 15 mm. thick) one containing .005 gm of crystallised violet and the other 10 gms. of potassium chromate both dissolved in 100 cc. of water.

The mean wave-length of the transmitted light is 650 $\mu\mu$. Yellow light was obtained from a sodium arc lamp which gives a wave-length of 589 $\mu\mu$. For the green light a mercury arc with a filter of three parallel walled glass vessels (each 15 mm. thick), one containing 10 gms. of potassium chromate, and each of the other two 0.025 gms. of potassium permanganate, each of them dissolved in in 100 c.c. of water was used. The transmitted wave-length is 546 $\mu\mu$.

OPTICAL PROPERTIES OF ANTHRAQUINONE

Anthraquinone crystal was previously regarded as belonging to the orthorhombic system but Sen from his X-ray studies (1940) found that it really belongs to the monoclinic system which was confirmed by goniometric and optical measurements. The *c*-axis, according to Groth's terminology, has been found to be the only symmetry direction and so this is one of the principal optical directions. The directions designated by *a* and *b* of Groth were considered, in conformity with the supposed orthorhombic character of the crystal, to be the other two principal axes. It was shown by Sen that for sodium light the real principal axes in this plane make an angle of 16° with

these two axes respectively. The results that have been obtained by us for the three different wave-lengths with the improved method of measurement are given in Table I.

TABLE I

Mean λ	Angle between Groth's 'a' axis and a principal optic direction	Semi-optic-axial angle
546μμ	15°35′40″	71°23′
589μμ	16° 5′40″	71°45′
656μμ	17°35′40″	72° 6′

The optic axial plane was found to be normal to the principal direction nearest to Groth's 'a' axis and the semi-optic-axial angle V is given in the third column of the Table I.

The refractive indices along the principal directions normal to the symmetry axis were determined by the Becke method and the other direction by utilising the value of V determined as above. The results are given in Table II. The refractive index along the principal direction nearest to Groth's 'a' axis has the highest value and hence it is designated as α according to the usual convention. The symmetry axis has the lowest refractive index which is accordingly designated as γ.

TABLE II

Mean λ	α	β	γ
589μμ	1·816	1·698	1·506
656μμ	1·806	1·690	1·500

These results indicate that the planes of the benzene rings are very close to the α-direction while they are nearer to the β-direction than to the γ-direction. These results agree with those obtained by Sen.

OPTICAL PROPERTIES OF *m*-DINITROBENZENE

Crystallographic data

Orthorhomb. Bipyr. V_h^{16}

$Z = 4$

$a = 13{\cdot}27$A, $b = 14{\cdot}06$A, $c = 3{\cdot}82$A.

Measurement.—Face angles of *m*-dinitrobenzene were measured by one circle goniometer and its axes were recognised. A single crystal with its *c*-axis (long axis) horizontal is placed on flat face *a* on Fedorov universal stage between the crossed nicols. The principal refractive indices, along the *b*-axis

and *c*-axis were determined by the method of disappearance of Becke line as described above.

Refractive index along the remaining principal direction was determined from the variation in refractive index with change of angular position in a symmetry plane of the triaxial ellipsoid.

The maximum and minimum refractive indices were found to be along the *c* and the *a*-axes respectively. The values of the principal refractive indices are given in Table III where α, β and γ according to convention represent refractive indices along the *c*, *b*, and *a*-axes respectively.

TABLE III

Mean λ	α	β	γ
546$\mu\mu$	1·434	1·707	1·842
589$\mu\mu$	1·432	1·766	1·839
656$\mu\mu$	1·430	1·764	1·835

OPTICAL PROPERTIES OF PHLOROGLUCINON DIHYDRATE

Measurement of the principal refractive indices were carried by the same method as that used for metadinitrobenzene.

The maximum and minimum refractive indices are along the *b* and the *a* axes respectively and hence according to usual convention α, β and γ represent the principal refractive indices along *b*, *c* and *a*-directions. The refractive indices are given in Table IV.

TABLE IV

Mean λ	α	β	γ
546$\mu\mu$	1·692	1·689	1·499
589$\mu\mu$	1·659	1·648	1·481
656$\mu\mu$	1·629	1·607	1·464

OPTICAL PROPERTIES OF NAPHTHALENE TETRACHLORIDE

The angle between the crystallographic axes and the principal axes in the plane (010) were measured in the same way as was done in the case of anthraquinone crystal. The angle between principal plane with *m*-face (110 or $1\bar{1}0$) is actually measured and from that angle with *a*-axis is calculated as angle between the *m*-face and the *a*-axis. The results are given in Table V.

TABLE V

Mean λ	Angle between a principle direction and 'a' axis
546μμ	2°16′
589μμ	1°28′
656μμ	0°34′

The three principal refractive indices were determined by the same method as in the cases of metadinitrobenzene and phloroglucine dihydrate the results are given Table VI.

TABLE VI

Mean λ	α	β	γ
546μμ	1·793	1·775	1·534
589μμ	1·786	1·766	1·528
656μμ	1·779	1·756	1·523

α_1, β and γ represent the refractive indices corresponding to the principal directions close to the *a* and *c*-axes and along the *b*-axis respectively.

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